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The SAMENS Method for Gold Nanostructure Syntheses: Green Synthesis and Electrocatalysis

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A glucose-starch based protocol - named the saccharide-based approach to metal nanostructure synthesis (SAMENS) - has been developed and expanded over the past years for the syntheses of metal [1-4] and mineral [5] nanocatalysts. The method enables the use of mild reaction conditions, e.g. < 100 °C, ambient atmosphere, aqueous buffer environment, neutral solution, and employs sustainable and renewable reducing and capping agents, e.g. glucose and starch.

Here, we describe the progress from the green syntheses of gold nanoparticles (AuNPs) using plant extracts to refined syntheses of anisotropic gold nanostructures, platinum nanoparticles (PtNPs), and gold-platinum core-shell nanoparticles (Au@Pt NPs), Fig.1.

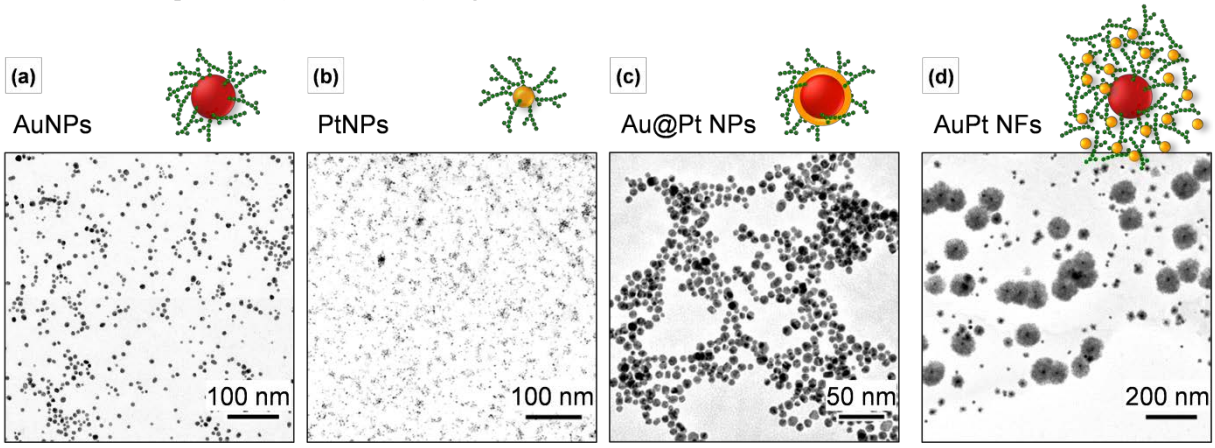

Fig. 1. Transmission electron micrographs of monometallic NPs, i.e. (a) AuNPs and (b) PtNPs, and (c) Au@Pt NPs and (d) gold-platinum nanoflower (AuPt NFs) bimetallic nanostructures, with inserted structure schemes. Red = Au, yellow = Pt, green = starch.

Extracts from abundant plant material, e.g. potato, carrot and onion, were used to successfully synthesize stable AuNP suspensions. Glucose and starch were identified as suitable candidates for reducing and capping agents present in the tested plant materials and AuNP synthesis. Acidic environments suppress deprotonation of aqua ligands substituted in the $[AuCl_4]^-$ complexes, a critical step in the reduction of the gold precursor. A range of biological and inorganic buffers were tested for the control of pH. Phosphate buffer (PB) and 2-(*N*-morpholino)ethanesulfonic acid (MES) were identified as optimal for fast formation of 12 and 8 nm AuNPs [1], and 2 nm PtNPs [2].

The starch-capped AuNPs were used to efficiently enhance the rate of interfacial electrochemical electron transfer of the heme protein cytochrome *c* (cyt *c*). In contrast to basal-plane graphite that interacts weakly with cyt *c* and Au(111) electrodes with too strong interaction, the starch-capped AuNPs facilitated close but gentle interaction leading to sustained electrochemical activity of the protein. The starch-capped PtNP catalytic activity towards dihydrogen oxidation, dioxygen reduction and hydrogen peroxide reduction was tested and the PtNPs found to show high activity for the latter similarly to Pt(111) electrodes. Furthermore, the PtNPs were loaded onto carbon supports and successfully tested as catalysts in a hydrogen fuel cell system.

By controlling the the metal precursor reduction conditions, two different gold-platinum bimetallic nanostructures were synthesized through sequential reduction of $[AuCl_4]^-$ and $[PtCl_6]^{2-}$. The nanostructures consisted of a AuNP core with a platinum-based exterior. Allowing the initially formed starch-capped AuNPs to “rest” (no stirring/heating) led to growth of the starch coating and incorporation of glucose. Subsequent addition and reduction of the platinum precursor caused formation of a few nm PtNPs trapped in the starch matrix around the AuNPs. This structure was denoted “nanoflowers” (AuPt NFs). Reducing the platinum precursor immediately after AuNP formation at 95 °C instead enabled the formation of

atomically thin Pt shells on the AuNP surface. The NPs were thoroughly characterized by cyclic voltammetry (CV), ultraviolet-visible light spectroscopy (UV-vis), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy mapping with scanning TEM (STEM-EDX), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA).

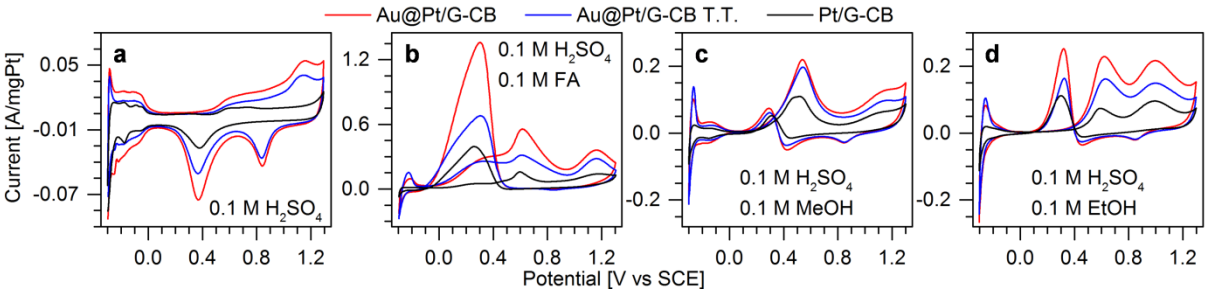

Fig. 2. Cyclic voltammetry of as-prepared Au@Pt NPs (red), Au@Pt NPs without starch (blue) and commercial PtNPs (black) in (a) pure electrolyte and electrolyte with (b) formic acid (FA), (c) methanol (MeOH) and (d) ethanol (EtOH). All catalysts are loaded on graphitized carbon black (G-CB). T.T. represents thermal treatment. Currents are normalized to Pt mass and scan rate 50 mV/s.

The intimate electronic interaction between the Pt shell and the Au sublayers led to a synergetic effect and altered catalytic reactivity of the platinum. The Au-Pt core-shell NPs (Au@Pt NPs) were loaded onto a graphitized carbon black (G-CB) support material and tested as fuel cell anode catalysts for the electrochemical oxidation of formic acid (FA), methanol (MeOH) and ethanol (EtOH), Fig. 2. The starch capping was successfully removed by a simple thermal treatment (1 h at 300 °C in air). This treatment resulted in restructuring and presumably contraction of the Pt shell, changing its catalytic activity. The specific electrochemical surface area (ECSA) of Pt was as high as 45-53 m^2/g .The electrocatalytic results showed a greatly increased performance over the commercial catalyst, comparable with recent results in literature. The core-shell structure provided better utilization of Pt, increased Pt activity through synergy between shell and core, and expected increased stability due to the larger particle size.

Acknowledgements

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